Section 5

COMPATIBILITY OF ALCOHOLS WITH OTHER FUELS IN BLENDS

Quick Reference Data

Impacts of Gasoline Composition on Methanol Solubility

Gasoline Composition (Volume %)			Minimum Temp. at Which	
Saturates	Aromatics	Olefins	10% Methanol will Dissolve	
100	0	0	27°C	(80°F)
65	21	14	7°C	(44°F)
43	2	55	-7°C	(20°F)
20	78	2	-16°C	(4°F)

Note: Ethanol and higher alcohols dissolve much more readily in hydrocarbons than methanol and can be added to a methanol/gasoline blend to increase methanol's solubility.

Low Temperature Solubility of Methanol in Gasoline

Aromatics in Gasoline (Volume %)	Methanol Solubility (Volume %) -23° to -18°C (-10° to 0°F)	Methanol Solubility (Volume %) 0° to 3°C (32° to 37°F)
16	2-3	5-10
28	5-10	15-20
31	5-10	>50
42	>50	>50

Effects of Adding Alcohol (Ethanol or Methanol) to Gasoline

- Increased volatility
- Volumetric expansion (small but measurable)
- Increased octane

Octane Ratings of Liquid Fuels

Compound	Octane Rating (R+M)/2
Gasoline	87-94
Ethanol	97
Methanol	98
MTBE	109
ETBE	110

Energy Content/Volume

Percent by Volume			
Ethanol (99.5%)	Gasoline (100%)	Lower Heating Value (Btu/gallon)	Relative Heating Value (Gasoline = 1)
0	100	109,000	1.000
10	90	105,662	0.969
20	80	102,324	0.938
30	70	98,986	0.908
100	0	76,000	0.697

Means for Overcoming Phase Separation

- Maintaining warm fuel mixture temperatures and low water content
- Using chemical additives
    - cosolvent alcohols
    - surfactants

Useful Terms and Definitions (also see Glossary)

- **Aromatics:** High octane blending components that have a benzene ring in their molecular structure. Commonly used term for the BTX group (benzene, toluene, xylene). Aromatics are hydrocarbons.

- **Azeotrope**: A liquid mixture that is characterized by a constant minimum or maximum boiling point which is different than that of any of the components. Azeotropes distill without change in composition.

- **Benzene Ring:** structural arrangement of atoms believed to exist in benzene and other aromatic compounds showing six carbon atoms in symmetrical hexagonal fashion.

- **Hydrogen Bond**: A bond between the hydrogen atom of one molecule and a pair of unshared electrons on the electronegative atom of another molecule.

- **Hydroxyl**: the chemical group or ion OH that consists of one atom each of hydrogen and oxygen, is neutral or positively charged and is characteristic especially of alcohols.

- **Octane Number (Rating)**: A measurement term used to identify the ability of a fuel to resist spontaneous combustion; the lower the octane rating the grater the tendency for a fuel to prematurely ignite due to heat and compression inside the cylinder and cause engine "knock."

    - ***Motor Octane:*** the octane as tested in a single cylinder octane test engine at more severe operating conditions. Motor Octane Number affects high speed and part throttle knock and performance under load, passing, climbing hills, etc. Motor Octane is represented by the designation M in the (R+M)/2 equation and is the lower of the two numbers.

    - ***Pump Octane:*** a term used to describe the octane as posted on the retail gasoline dispenser as (R+M)/2 and is the same as Antiknock Index.

    - ***Research Octane:*** the octane as tested in a single cylinder octane test engine operated under less severe operating conditions. Research Octane Number affects low-to-medium speed knock and engine run-on. Research Octane is represented by the designation R in the (R+M)/2 equation and is the higher of the two numbers.

- **Olefins**: unsaturated open-chain hydrocarbons containing at least one double bond; member of the ethylene series.

- **Phase Separation**: the formation of layers due to the presence of water within a low level alcohol-gasoline blend, with most of the hydrocarbons in the upper layer and water, alcohol, and some aromatic hydrocarbons in the lower level. This condition can lead to driveability problems.

- **Solubility:** the amount of a substance that will dissolve in a given amount of another substance and is typically expressed as the number of parts by weight dissolved by 100 parts of solvent at a specified temperature and pressure or as percent by weight or by volume.

Key Issues and Implications

Issues and Implications

Issue #1: Solubility of Methanol in Gasoline

Methanol is not completely soluble in those gasolines which contain low levels of aromatic compounds, particularly at low ambient temperatures. New efforts to reformulate gasoline are likely to result in reduced levels of aromatic compounds in gasoline (primarily because of the carcinogenic character of these compounds), which may exacerbate this problem.

Implications of the Low Methanol Solubility:

- In flexible fuel vehicles (FFVs), as you switch between methanol (M85) and reformulated (low aromatic content) gasolines, solubility problems may occur.

Solutions to the Solubility Problem:

- In order to avoid operational problems with FFVs, it may be necessary to use ethanol or "higher" alcohols (which dissolve more readily in gasoline) as additives to methanol fuels to improve solubility with gasoline.

Detailed Information: Refer to pages 5-2 through 5-3.

Issues and Implications (Continued)

Issue # 2: Phase Separation

In alcohol/gasoline blends, the presence of water (even in small amounts) can lead to "phase separation" -- the formation of layers within the fuel or storage tank, with most of the hydrocarbons in the upper layer and water, alcohol, and some aromatic hydrocarbons in the lower level. This problem is most pronounced in low-level alcohol blends and at low ambient temperatures.

Implications of Phase Separation:

- **Phase separation of blends can lead to fuel line freezing or poor driveability.** In flexible fuel vehicles (FFVs), the presence of water in the fuel mixture can cause the optical fuel sensor to malfunction, which could lead to driveability problems.

Potential Solutions :

- A number of approaches are available to prevent phase separation, including: improved maintenance of gasoline storage and distribution systems; the use of additives (such as higher or "heavy" alcohols or surfactants) that will prevent separation even when water is present in a blend; and water removal facilities at fuel dispensing stations.

Detailed Information: Refer to pages 5-7 through 5-10.

Section 5
COMPATIBILITY OF ALCOHOLS WITH OTHER FUELS IN BLENDS

- Solubility in Gasoline
- Creation of Mixtures Having Different Properties than Constituent Fuels
- Bonding with Water and its Implications
- Alcohol/Gasoline Separation
- Methods to Overcome Phase Separation

Introduction

Although ethanol and methanol are completely soluble in water, their solubility in gasoline varies depending on both temperature and gasoline composition. Adding ethanol or methanol to gasoline results in mixtures having different properties than the constituent fuels. In addition, alcohol/gasoline blends have less energy content than pure gasoline. In relatively dilute blends (less than 20%), alcohols contribute to:

- increasing the octane number and the vapor pressure of the blend,
- depressing the boiling temperature of gasoline; and
- a small but measurable volume expansion.

Alcohol/gasoline blends are sensitive to the presence of small amounts of water, even at room temperature. Because of their polar structure, ethanol and methanol molecules actively associate with water molecules through hydrogen bonds.

This can result in the separation of the gasoline/alcohol blend into two phases. Paraffinic hydrocarbons predominate in the upper phase, while the lower phase consists primarily of alcohol, water and small quantities of aromatic hydrocarbons. A strategy to prevent the occurrence of phase separation of alcohol/gasoline blends is presented at the end of this section.

Solubility in gasoline

Gasoline is a mixture of petroleum-derived hydrocarbons and specialized additives. Its composition varies, depending on the desired octane rating, the nature of the base petroleum feedstock, the season of the year, and a variety of other factors. Over the past 20 years, there has been a pronounced trend in the United States toward the use of more aromatic hydrocarbons (benzene, toluene and xylene) in the gasoline pool. Although these compounds vaporize readily and are inexpensive to produce, aromatic hydrocarbons pose serious health hazards and contribute to urban air pollution. Therefore, efforts to "reformulate" gasoline normally include a major reduction in the percentage composition of aromatics. Alcohols and alcohol-based ethers blend more easily with certain types of gasoline components than others. This is particular true for low molecular-weight alcohols such as methanol.

Policy Issue #1

> Methanol and non-aromatic hydrocarbons are not very soluble in each other, and solubilities decrease as temperature is lowered. In addition, the solubility of methanol in gasoline is affected by the chemical nature of the hydrocarbons making up the gasoline. Methanol dissolves less readily in paraffinic hydrocarbons (such as n-octane, n-hexane and cyclohexane) than it does in aromatic hydrocarbons (such as benzene and toluene).

Solubility is not a problem for alcohol/gasoline blenders today, since ethanol and high aromatic feedstocks are used. However, if methanol is used as an octane enhancer in the future, solubility maybe jeopardized in cold climates, as shown in Table 5-1 below. [1]

Table 5-1
Solubility of Methanol in Gasoline

Aromatics in Gasoline, Volume Percent	Methanol Solubility, Volume Percent -23° to -18°C (-10° to 0°F)	0° to 3°C (32° to 37°F)
16	2-3	5-10
28	5-10	15-20
31	5-10	>50
42	>50	>50

Gasoline Composition Saturates	Aromatics	Olefins	Minimum Temperature at which 10% Methanol will Dissolve, °C (°F)
100	--	--	27 (80)
65	21	14	7 (44)
43	2	55	-7 (20)
20	78	2	-15 (4)

For gasolines with 16% aromatics, for example, 5-10% methanol is soluble at temperatures above 0°C (32°F), and 2-3% is soluble at temperature as low as -23°C (-10°F). This will be important for methanol blending with reformulated gasolines, which are expected to contains as little as 20% aromatics (current gasolines contain 30-34% aromatics on average). In addition, flexible fuel vehicles (FFVs) will have to have the ability to switch readily from one fuel (such as M85) to another (such as reformulated gasoline). Both fuels will be present in the fuel tank after the switch is made. Therefore, issues of solubility and fuel compatibility will be more important for FFVs than for dedicated fuel (i.e., M85) automobiles. The addition of cosolvents and other additives can help resolve this potential problem.

Ethanol and higher alcohols such as isopropanol and 1-butanol dissolve more readily in hydrocarbons found in gasoline than does methanol, and they can be added to a methanol/gasoline blend to increase methanol's solubility. Discussions of gasoline/alcohol "blends" generally refer to gasoline/ethanol combinations (because of the difficulties associated with blending lower concentrations of methanol in gasoline) or gasoline mixed with other oxygenates such as alcohol-based ethers (MTBE and ETBE).

Creation of Mixtures Having Different Properties than Constituent Fuels

Volume Change of Alcohols/Gasoline Blends

When ethanol and methanol are added to gasoline, a small but measurable volume expansion effect occurs, as illustrated in Figure 5-1. [2] The expansion of a gasoline/methanol blend reaches a maximum value of about 0.2% over a broad range of concentrations from about 20 to 80% methanol. Ethanol/gasoline blends reach about the same maximum expansion but peak sharply at about 10-20% ethanol content. Expansion values for gasoline/ethanol blends as high as 0.55% with a 12.5% concentration of ethanol have been observed.

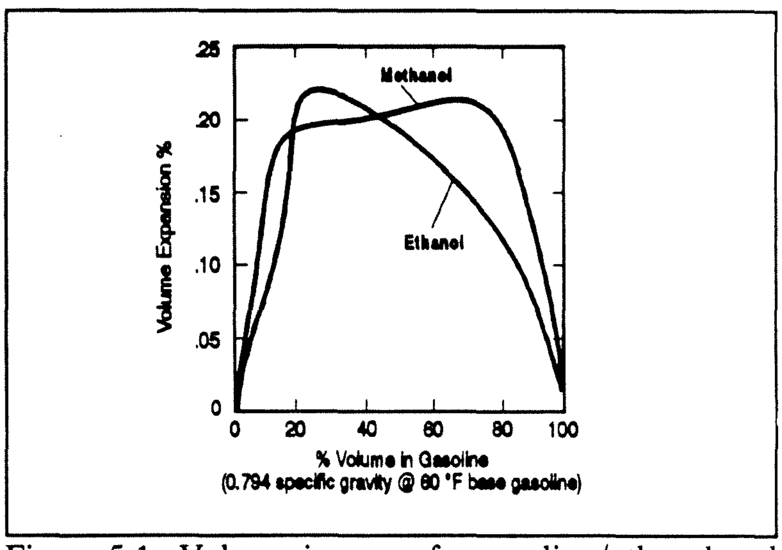

Figure 5-1., Volume increase for gasoline/ethanol and gasoline/methanol blends.

Increased Octane Rating

Alcohols and alcohol-based ethers have much higher octane ratings than most gasolines as seen in Table 5-2 below. [3]

Table 5-2. Octane ratings of gasoline and oxygenates

Compound	**Octane Rating (R+M)/2**
Gasoline	87
Ethanol	97
Methanol	98
MTBE	109
ETBE	110

When blended with gasoline, alcohols and alcohol-based ethers contribute to increasing the octane number of the blend. In fact, the "blending" octanes of alcohols are higher than their octane ratings would indicate. Methanol has a blending octane of 115 at 5% volume in gasoline, and ethanol is rated at 111 at 10% in gasoline. [4] The use of 10% ethanol will increase the octane number of a base gasoline from 2.5 to 3 octane points. [5] The influence of alcohol additions on four base gasoline stocks -- straight run, catalytically cracked, thermally cracked, and polymer gasoline -- is shown in Figure 5-2. [6]

In addition to the octane data shown, the curves in Figure 5-2 reveal that the greatest improvement in octane number from alcohol addition is obtained for gasoline stocks of the lowest octane number (straight run and thermally cracked), as would be expected.

Reduced Energy

Since the heating value (also called "energy content/volume") of ethanol is 76,000 Btu/gal or about two-thirds of that of gasoline (109,000 - 119,000 Btu/gal), blends of these fluids will also have less energy than gasoline, as shown in Table 5-3. [7]

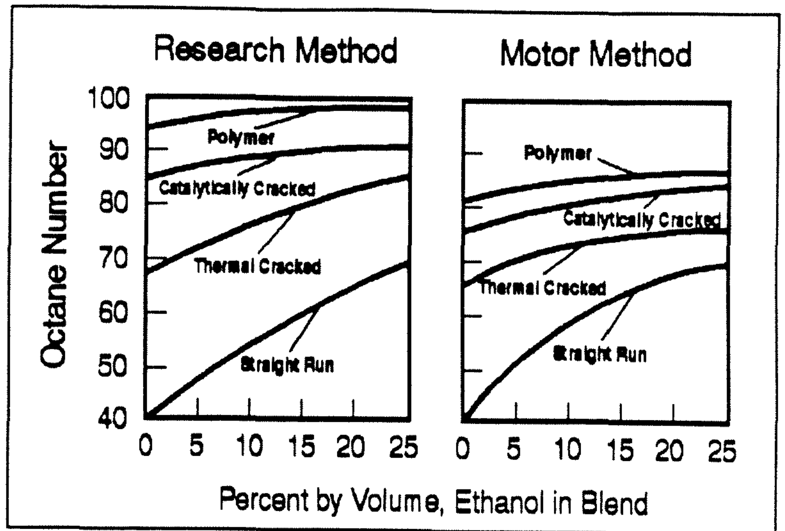

Figure 5-2., Increase of octane ratings of several gasoline stocks with the addition of ethanol.

Table 5-3 Calorific Values of Ethanol-Gasoline Blends

Percent by Volume Ethanol (99.5%)	Gasoline (100%)	Lower Heating Value Btu/gal	Relative Heating Value (Gasoline = 1)
0	100	109,000	1.000
10	90	105,662	0.969
20	80	102,324	0.938
30	70	98,986	0.908
100	0	76,000	0.697

This reduced energy per unit of volume will require increased fuel flow rates for proper engine operation. When fuels of different heating value are being considered, the energy of the fuel per unit volume is as equally important as the air-fuel mass ratio. Therefore, if a high percentage alcohol/gasoline blend is substituted for gasoline in an automobile, larger metering jets may be required to maintain the same percent of the stoichiometric air for combustion, or the same equivalence ratio. Up to 20% ethanol blends are normally accommodated by current production vehicles without modifications, and flexible fuel vehicles are designed to accept any alcohol/gasoline mixture ratios without difficulty.

Bonding with Water and its Implications

Low-molecular weight alcohols such as methanol and ethanol are completely soluble in water. Because of their polar structure, the alcohol molecules actively associate with water molecules through hydrogen bonds. The hydrogen bonds are strong enough to prevent the separation of the water/alcohol mixture by distillation.

Distillation of a solution of ethanol and water will not yield ethanol more concentrated than 95%. A mixture of 95% ethanol and 5% water boils at a lower temperature (78.15°C) than either pure ethanol (boiling point or bp = 78.3°C) or pure water (bp = 100°C). Such a mixture is called an "azeotrope." Pure ethanol is often obtained by adding benzene to the mixture of 95% ethanol and water and then distilling this solution. Benzene forms a different azeotrope with ethanol. This azeotrope boils at 64.9°C, leaving behind the water (along with traces of ethanol). Eventually, pure ethanol (also called absolute or neat alcohol) is produced by continued distillation after the benzene azeotrope is vaporized.

The earlier difficulty of producing water-free (anhydrous or absolute) alcohol explains why older engine tests were usually run with alcohol containing some water. In more recent years, it has become practical to produce alcohol with less than 0.1% water at an acceptable cost, ending the use of the 95% product in fuel applications.

Alcohol/Gasoline Separation

The solubility of methanol and ethanol in gasoline in the presence of even a small quantity of water is very limited. Even at room temperatures, only 1-2% of water can be tolerated for 25-40% alcohol mixtures before phase separation occurs and this tolerance drops sharply at lower temperature and at lower alcohol contents, as shown in Figures 5-3 and 5-4. [8,9] Although both of fuel alcohols have low water tolerance, methanol is somewhat less tolerant of water than ethanol in the 10-20% blending ratios.

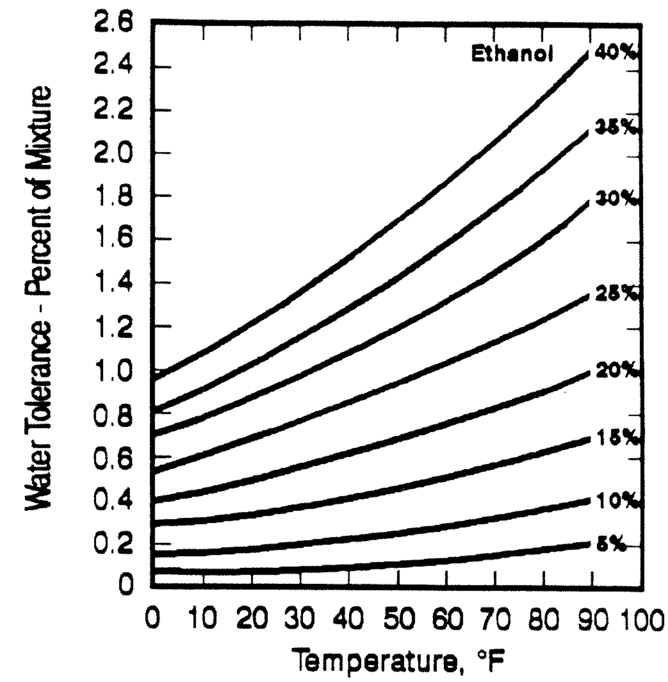

Figure 5-3., Water tolerance of ethanol/gasoline blends.

Policy Issue #2

When small amounts of water are added to ethanol/gasoline or methanol/gasoline blends, hydrogen bonds form between the water and alcohol molecules, and the blend separates into two phases. Paraffinic hydrocarbons (such as n-hexane and cyclohexane) predominate in the upper phase, while the lower phase consists primarily of alcohol, water, and small amounts of aromatic hydrocarbons. The beginning of this separation is characterized by a cloudiness or "haze" in the mixture. The ability of the blend to carry moisture without separation increases when more alcohol is present, and when temperature is increased. Phase separation was a serious problem in early years of gasohol (10% ethanol, 90% gasoline) usage because the older one-stage distillation process did not remove all of the water. Under winter conditions, phase separation could lead to frozen fuel lines and difficult starting. Current production practices routinely produce anhydrous or water-free fuel ethanol, largely eliminating the problem of phase separation.

The amount of water that can be tolerated by a 25% ethanol/gasoline blend at room temperature is about 1%. If twice this amount is added to a sample of 25% blends, most of the alcohol will separate from the gasoline in a few seconds and settle to the bottom of the container. The interface between ethanol and gasoline will be sharply defined. Given the current limited use of fuel ethanol in the United States and modern production techniques, water intrusion has not been a serious issue.

For methanol, however, the presence of water is a more serious problem. Data on the water sensitivity of methanol/gasoline blends are given in Figure 5-4. A blend containing 10% methanol must be protected against water in concentrations greater than about 0.05 - 0.2% (depending on the fuel's temperature) or the blend will separate. To create a national production and distribution system, new dedicated pipelines and storage tanks will be required. Gasoline as conventionally transported, however, is often exposed to water in volumes greater than 1 percent.

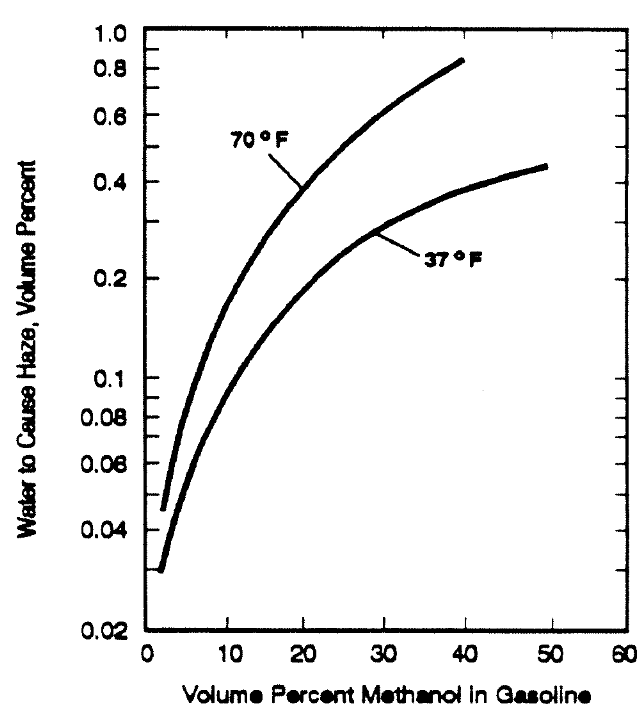

Figure 5-4., Methanol/gasoline blends tolerate little water.

The evidence of water intrusion in the existing fuel distribution system has been well documented. [10] Some of this water results from the condensation of moisture from the air in vented and partially filled tanks, and when products containing water are shipped by pipeline. But most of the water contamination is thought to result from precipitation penetrating the seals of floating roofs of bulk storage tanks.

Methods to Overcome Phase Separation

Considerable research has been undertaken in the last two decades to identify efficient means to stabilize alcohol/gasoline blends while preserving the other favorable characteristics of the fuel. [11,12,13,14] Several strategies have been proposed to monitor and control phase separation, and are presented in a recent review paper. [15]

Policy Issue #2

Keeping the mixture temperature high and the water content low improves the compatibility of gasoline/water/alcohol mixture. The phase separation problem can be effectively controlled by current technology, but at a substantial cost. The use of chemical additives to prevent phase separation has been extensively studied and successfully applied. The most popular additives are cosolvent alcohols (C_2-C_{12}) and various commercial noniomic surfactants and various anionic fatty acid surfactants. Among cosolvents alcohols, linear alcohols are more efficient than branched ones, and their efficiency increases with the carbon chain length. Iso-propanol, 1-butanol, n-decanol and palmitic acid have been suggested by several authors as the most cost-effective phase separation inhibitors.

ENDNOTES:

1. American Petroleum Institute, "Alcohols: A Technical Assessment of Their Application as Fuels." API Publication No. 4261, Second Edition, July 1988.

2. Scheller, W.A., and B. J. Mohr, "Gasoline Does Too, Mix with Alcohol," *Chemtech*, Vol. 7 (1977), pp. 616-623.

3. American Petroleum Institute, op.cit.

4. Pahl, R.H., "The Roles of Ethers in Meeting Air Quality in America," Conference on Air Quality Issues in American Motor Fuel Business, Information Resources, Inc., November 15-17, 1988.

5. Johnson, Larry "Vehicle Performance and Air Quality Issues of 10% Ethanol and 90% Gasoline Blends." Paper presented at the "International Forum on Energy Engineering." The 24th Intersociety Energy Conversion Engineering Conference, Washington, D.C. August 6-11, 1989.

6. Bolt, Jay A., "A Survey of Alcohol as a Motor Fuel" SAE PT-80/19.

7. Tshiteya, Rene M., Calculated Values.

8. Bolt, op.cit.

9. Ingamells, J. C. and Lindquist, R. H., "Methanol as a Motor Fuel or Gasoline Blending Component" SAE 750123, Automotive Engineering Congress and Exposition, Detroit, MI, February 1975.

10. Sperling, D., *New Transportation Fuels. A Strategic Approach to Technological Change*. University of California Press. Berkeley and Los Angeles, California, pp. 221-224, 1988.

11. Patel, R. S., and M. Cheung, "Effects of Heptanoic and Oletic Acids on the Phase Separation Temperatures of Methanol/Hydrocarbon/Water Mixtures." Energy & Fuels 3 (1989).

12. Lee, H. K., D. O. Shah, and N. D. Brinkman, "Enhancing Low-Temperature Phase Stability of a 50/50 Methanol/Hydrocarbon Blend," SAE paper 881680, 1988.

13. Anwar-ul-Hag, M., "Phase Separation of Methanol/Gasoline Blend. Part II." *Pakistan J. Sci. Ind. Res.*, Vol. 30, No. II (November 1987), pp. 815-816.

14. Nakayama, M., "Water Tolerability of Methanol-Gasoline Blends (Phase Separation and SI Engine Performance)." SAE Paper 85220, 1985.

15. Tshiteya, Rene M., Vermiglio, Ezio and Onstad, James "The Impact of Phase Separation in Alcohol/Gasoline Blends on the Existing Fuel Distribution System." Paper accepted for publication and presentation at the 25th Intersociety Energy Conversion Engineering Conference, in Reno, Nevada, August 12-17, 1990.